Comparison of coagulant type on natural organic matter removal using equimolar concentrations
Rolando Fabris, Christopher W. K. Chow and Mary Drikas

ABSTRACT
Research has shown that in drinking water sources there is a portion of the natural organic matter (NOM) that is recalcitrant to coagulation, regardless of the treatment conditions applied. Advances in inorganic coagulants have resulted in the emergence of many pre-polymerized formulations which may demonstrate improved coagulation performance. The aim of this study was to determine the effects of several coagulant types on dissolved organic carbon (DOC) removal where the molar concentrations of the metal ions were comparable. In the second stage, this work also investigated selected coagulants to determine whether improvements in coagulation conditions or alternative coagulants will be sufficient to remove problematic components in the organic matter responsible for disinfection demand and disinfection by-product (DBP) formation in a high DOC water source. When compared at equimolar concentrations, advanced coagulants were found to perform equally for DOC removal as traditional inorganic coagulants. While they did not necessarily target or improve removal of recalcitrant NOM and DBP precursors, they successfully demonstrated broader conditions at which coagulation was effective, reducing the reliance on precise optimization strategies. Coagulation remains a well developed and cost effective means of water treatment, with continuing relevance into the foreseeable future.

Key words | alum, coagulation, disinfection by-products, ferric chloride, poly-ferric sulphate

INTRODUCTION
The efficiency of a water treatment process for drinking purposes is usually associated with physical water quality parameters such as colour and turbidity. However, it has become widely accepted that the treatability of water is primarily influenced by the natural organic matter (NOM) present in water and changes in its character.

Inorganic metal coagulants have long been used in the treatment of water for drinking purposes. Enhanced coagulation, whereby higher doses of coagulant, with or without pH control, are applied has demonstrated improved removal of NOM (Kavanaugh 1978; Gregor et al. 1997; White et al. 1997; van Leeuwen et al. 1999). However, associated research has shown that in most cases there is a portion of the NOM that cannot be removed by coagulation, regardless of the treatment conditions applied (Randtke 1988; Edwards 1997; Chow et al. 1999; van Leeuwen et al. 2002). This portion of the organic matter can be referred to as being recalcitrant NOM. These compounds can result in poor or inconsistent disinfectant residual, disinfection by-products (DBPs), bacterial regrowth and membrane fouling. From a future focused water quality perspective, it is important to identify whether or not these recalcitrant materials make a significant contribution to the problems discussed above and whether there is a genuine need to apply improved techniques to aid in their removal. If their further removal is desired, amongst the easiest methods that may be implemented into existing conventional treatment plants is improvement in the applied coagulant. While processes may need to be optimized for a new coagulant, it will not likely require extensive changes to existing infrastructure and is therefore a viable economic option.
Ferric and aluminium based coagulants, although operating by similar mechanisms (Vik et al. 1985; Dentel & Gossett 1988; Hundt & O’Melia 1988; Randtke 1988; Dennett et al. 1996), differ mostly by the pH range in which they operate. Literature and past work by the authors has shown that coagulants perform best at or near their isoelectric point (Vik et al. 1985; Hundt & O’Melia 1988; Randtke 1988; Lefebve & Legube 1990; Edwards 1997; Gregor et al. 1997; White et al. 1997; Vrijenhoek et al. 1998). For aluminium based coagulants, this is at or near pH 5.5, while for ferric coagulants it is closer to pH 4.5. Although most coagulants act as an acidic species and lower the pH at which treatment occurred, aluminium based coagulants typically start operating within their optimum pH range at lower doses than ferric coagulants. When enhanced treatment conditions are employed, effects of different optimum pH ranges should be diminished and the coagulants can be compared more easily on their ability to remove dissolved organic carbon (DOC).

Advances in inorganic coagulants have progressed steadily in recent times with the majority of work based around pre-polymerized preparations of the traditional aluminium and iron salts. Through controlled production conditions, the formation of desired metal-hydroxy complexes of higher specific charge is increased, which may demonstrate improved coagulation performance. The advantages over traditional inorganic coagulants can include a wider operating pH range, less temperature sensitivity and lower dose requirement (Jiang & Graham 1998a). Amongst the advanced coagulants, poly-aluminium chloride (PACl) has been most extensively researched and is used in many countries around the world. While characterization of dissolved species and its turbidity removal is well understood (Jiang & Graham 1998a; Gregory & Dupont 2001; Gregory & Rossi 2001; Gao et al. 2002b), little has been reported concerning DOC removal. However, previous work (Volk et al. 2000) has shown that under enhanced coagulation conditions (lower pH), ferric coagulants perform better for the removal of NOM than both alum and PACl. Poly-ferric sulphate (PFS) has been well characterized and reported (Jiang et al. 1996; Jiang & Graham 1998b; Cheng 2002; Cheng & Chi 2002) and has shown improved treatment performance for humic acids (Cheng 2002; Cheng & Chi 2002) and DOC (Jiang et al. 1996).

More recent developments in advanced coagulants have focused on the stabilization of the floc particle, usually through incorporation of silica into the hydroxy complex structures, such as poly-aluminium silica sulphate (McGregor 2002), poly-aluminium silica chloride (Gao et al. 2002a) and poly-ferric silica chloride (Wang & Tang 2001). These are focused on better removal of turbidity and improved floc handling properties. However, these coagulants are not targeted towards DOC removal. Gao et al. (2002b) noted that aluminium silica polymer composites enhanced aggregating efficiency but weakened charge neutralization effectiveness in coagulation processes.

Several studies into comparisons of the performance of various coagulants have been performed but few have eliminated the effects of molar concentration (Crozes et al. 1995; Hering et al. 1996; Jiang et al. 1996; Edwards 1997). Typically, when comparing the performance of various coagulants for a given dose, it is difficult to determine whether the improved performance is due to superior coagulation, or because of differences in the coagulant’s metal ion concentration. For example, there is approximately twice the concentration of the metal ion in a ferric salt as there is in an equivalent aluminium salt for a given coagulant dose.

The aim of this study was to visually map the effects of coagulant type on DOC removal where the molar concentrations of the metal ions (aluminium and iron) were the same. As an additional component, investigations were conducted to determine whether improvements in coagulation conditions or alternative coagulants could remove the components in the organic matter that cause secondary issues such as loss of disinfection residual and DBP formation.

**METHODS**

**Source waters**

Two local reservoir waters were chosen for this work, Hope Valley and Myponga. Generally, Hope Valley is regarded as a medium colour, medium DOC water while Myponga is regarded as a high colour, high DOC water. These water sources were chosen on the basis of their ease of availability and because they represent examples of a primary surface water catchment (Myponga) and an artificial secondary surface water catchment (Hope Valley). In order to eliminate the effects of differing alkalinity on how the waters reacted...
to coagulant dosing and pH correction, alkalinity as sodium bicarbonate was added to Myponga Reservoir water to bring it to the same level as Hope Valley water. Water quality at the time of the investigation is shown in Table 1. The higher specific UV absorbance (SUVA) of Myponga Reservoir relates to greater conjugated (aromatic) organic functionality (Weishaar et al. 2003), suggesting a greater degree of treatability.

### Chemicals

Four coagulants, aluminium sulphate (Hope Valley WTP), poly-aluminium chlorohydrate (PAC-AC, Hardman, Australia), ferric sulphate (Deltrex, Australia) and ferric chloride (Profloc-F, Orica Watercare, Australia) were selected to treat the two local reservoir waters. Doses were applied as equimolar concentrations of the metal ion with respect to alum, ranging from 20 to 120 mg/L. The treatment options included conventional and enhanced coagulation. In addition, coagulation was performed at pH levels ranging from 3 to 8, achieved through the addition of 0.2 M solutions of HCl and NaOH (AR Grade, APS Finechem). Target pH was achieved by determination of acid or base requirement by prior titration of a 500 mL volume of the raw water containing the coagulant dose.

In the second stage of the investigation, Myponga Reservoir was coagulated using alum and ferric chloride as controls and compared to a pre-polymerized iron based coagulant, PFS that was developed specifically for improved DOC removal (Jiang et al. 1996).

### Experimental conditions

Jar tests were performed on a six paddle gang stirrer (SEM Pty Ltd, Australia) in 2 L gator jars (B-KER², Phipps & Bird, USA). Samples were flash mixed at 200 rpm for 1 min followed by 14 min of slow mixing at 25 rpm and 15 min of settling before samples were gravity filtered through 11 μm pore size paper filters (Grade 1, Whatman International Ltd, UK) to simulate rapid sand filtration.

### Instrumental analyses

Measured parameters included pH, DOC, 72 h chlorine demand, trihalomethane formation potential (THMFP), rapid fractionation and residual metals. Measurement of pH was performed using a portable pH meter with a sealed, gel filled reference electrode with temperature compensation (pH320, WTW, Germany). The use of a portable meter allowed pH during the jar tests to be monitored in situ if required. DOC was measured on a Sievers 820 total organic carbon detector (Ionics Instruments, USA). Residual metals were analysed externally by ICP-MS. Chlorine demand was determined by the addition of 20 mg/L Cl₂ to 150 mL of sample and storage at room temperature (20 °C) in the dark. Residual chlorine was titrated after 72 h by the DPD ferrous titrimetric method (APHA et al. 1998) and the demand calculated by the difference. THMFP was determined by the addition of 20 mg/L Cl₂ to 40 mL of pre-warmed (30 °C) sample in a brown glass bottle with no headspace. Reaction was allowed for 4 h at 30 °C in a covered water bath before quenching the residual chlorine with excess ascorbic acid. THM concentrations were determined by purge and trap gas chromatography with electron capture detection. Rapid fractionation technique separates DOC into four fractions based on character and hydrodynamic size. Fractions produced are defined as very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilics (CHA) and neutral hydrophilics (NEU). Specifics of the technique and definitions have been described elsewhere (Chow et al. 2004).

### Table 1 | Investigated water quality of Hope Valley and Myponga reservoirs

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>Colour (HU)</th>
<th>UV&lt;sub&gt;254&lt;/sub&gt; (/cm)</th>
<th>DOC (mg/L)</th>
<th>SUVA (/m/mg/L)</th>
<th>Alkalinity (mg/L as CaCO₃)</th>
<th>Aluminium (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hope Valley</td>
<td>8.1</td>
<td>2.76</td>
<td>17</td>
<td>0.135</td>
<td>5.1</td>
<td>2.65</td>
<td>100</td>
<td>0.18</td>
</tr>
<tr>
<td>Myponga</td>
<td>7.6</td>
<td>3.51</td>
<td>103</td>
<td>0.577</td>
<td>14.8</td>
<td>3.90</td>
<td>54&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.16</td>
</tr>
</tbody>
</table>

<sup>a</sup>Alkalinity of Myponga adjusted to match Hope Valley prior to testing.

212 R. Fabris et al. Comparison of coagulant type on NOM removal
Journal of Water Supply: Research and Technology—AQUA | 61.4 | 2012
RESULTS AND DISCUSSION

Treatment performance indicators

To demonstrate the combined effects of coagulant dosing and pH effects on DOC removal, data were combined to create two-dimensional contour plots. Using these plots, trends can be visually examined across both the pH and dose range. Any combination of the treatment conditions applied can be evaluated for their ability to remove DOC. Lighter shaded regions indicate areas of improved DOC removal and cover all conditions within the applied dose and pH range where similar removal can be expected.

Parameters such as colour and UV absorbance are closely related to DOC concentration. In addition, coagulant doses for effective turbidity removal are generally less than those for effective DOC removal. Therefore, it is logical to assume that improvements in DOC removal will also produce reduction of colour and UV absorbance and generally better water quality. The advantage of these plots is the ability to ‘map’ the behaviour of a coagulant for particular water sources. This allows the prediction of how changes to treatment conditions would affect DOC removal and therefore overall water quality without the need for further incremental jar testing.

While it may seem counterintuitive for metal residuals to increase with decreasing dose (Figures 1 and 2), this is indicative of the fact that at suboptimal doses, coagulation is not efficiently promoted, hence higher amounts of the coagulant remain in solution. In treatment of Myponga with the aluminium coagulants (alum and PACl), higher doses and pH above 6 is required to meet the guidelines for aluminium residuals in the treated water (Figure 1), with pH above 5 required for the ferric coagulants (Figure 2). Unlike aluminium salts, ferric coagulants exhibited a greater dependence on high doses to maintain low
metals residuals, especially ferric sulphate. When correlated with the DOC removal data, it was shown that to achieve optimal DOC removal with low metal residuals requires select and carefully controlled conditions, even for PACl that typically allows less reliance on pH control for effective treatment. For Hope Valley (Figures 3 and 4), the increased specific dose (coagulant per mg DOC) for the dose range applied resulted in broader areas of effective coagulation and hence broader areas where metal residuals fell below the guideline values.

In the evaluation of a coagulant’s ability to remove NOM from a water source, it is important to examine both quantitative and qualitative aspects of the coagulant and also the treated water. The most basic and fundamental criterion is the amount of overall DOC removal. While the coagulants were applied in a dose range covering under-dosing through to over-dosing conditions at a fixed pH of 6.2, it was clear that in all cases, once an adequate dose was achieved, manipulation of the coagulation pH was more effective for DOC removal than manipulation of the dose. Table 2 summarizes the maximum DOC removals achieved for the applied coagulants and the respective conditions. The ferric coagulants exceeded 70% DOC removal in both waters but required particularly low pH conditions to achieve this. Based on a representative bulk chemical cost, ferric sulphate was also the most economic coagulant, costing 4 cents per megalitre treated at the optimum dose; however this does not account for the additional chemicals required for pH correction. PACl was the most expensive coagulant and showed the least DOC removal; however other operational benefits besides DOC removal may drive the preferred application of PACl for different water sources.

**Disinfection performance indicators**

In the second stage of the investigation, alum and ferric chloride were also compared to a pre-polymerized iron based coagulant, PFS. It was these data that were
investigated for secondary water quality parameters such as disinfectant demand and THMFP. Organic characterization was applied to describe the differences. In coagulation tests PFS was found to be roughly equivalent in performance to ferric chloride. For the Myponga Reservoir source water, an apparent maximum DOC removal around 77% may indicate the theoretical best removal achievable by any isolated coagulation process.

In comparing the effectiveness of the coagulants to remove problematic organic components, rapid fractionation, Cl₂ reactivity and THMFP were employed. Through the application of these analyses, it could be determined if the alternative coagulants applied were better at reducing these secondary water quality parameters and which character fractions were most likely responsible. Analysis of the treated water by rapid fractionation showed some distinct differences in the ability of the coagulants to remove character fractions of the source water (Figure 5). Previous work (Dennett et al. 1996) has shown that ease of removal of the fractions by coagulation were CHA > VHA = SHA > NEU. This trend is also exhibited for the source waters and inorganic coagulants applied in this study. Ferric chloride and PFS showed a roughly equivalent performance to each other and were notably superior to alum. The pre-polymerized coagulant, PFS, showed marginally better recalcitrant organic matter (hydrophilic neutral) removal than ferric chloride in Myponga Reservoir water.

Figure 6 shows the relationship between the applied coagulant dose and chlorine demand (72 h) plus applied coagulant dose and THMFP. Comparison of chlorine demand with THMFP results indicates that there is little discernable relationship, with the trends and order of the coagulants not showing consistent behaviour. Generally, the treatments with ferric coagulants exhibited lower chlorine demand, due largely to lower treated water DOC. Results indicate that as coagulant dose increases there is

Figure 3  |  Hope Valley % DOC removal and aluminium residuals contour plots for alum and PACl. NHMRC and US-EPA guideline is 0.2 mg/L aluminium. Doses are expressed as equimolar metal ion concentration with respect to alum.
little improvement in the removal of components of the NOM that are reactive with chlorine. Once a critical minimum coagulation dose was achieved, improvement in chlorine demand was marginal despite small improvements in DOC removal with increasing dose. For the ferric coagulants, this minimum dose was approximately 20 mg/L higher than alum (Figure 6(a)) with detrimental effects on the chlorine demand at the lowest dose due to poor flocculation (Figure 6(b)); however THMFP reduction at these low doses was still effective. This highlights the mechanistic differences between bulk chlorine reactions with NOM and the formation of THMs. In terms of chlorine demand per unit DOC (data not shown), increasing values at higher doses relate to preferential removal of

Table 2 | Highest DOC removal conditions for applied coagulants with Myponga Reservoir with coagulant cost (AUD) to treat 1 ML at the optimum dose

<table>
<thead>
<tr>
<th>Applied coagulant</th>
<th>Coagulant formula</th>
<th>Myponga best condition</th>
<th>Myponga % DOC removal</th>
<th>Cost per ML (AUD)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium sulphate</td>
<td>Al₂(SO₄)₃·18H₂O</td>
<td>100 mg/L pH 5</td>
<td>63</td>
<td>0.045</td>
</tr>
<tr>
<td>Poly-aluminium chloride</td>
<td>AlₙClₙ₋ₘ(OH)ₘ</td>
<td>120 mg/L pH 6</td>
<td>62</td>
<td>0.081</td>
</tr>
<tr>
<td>Ferric sulphate</td>
<td>Fe₂(SO₄)₃</td>
<td>120 mg/L pH 4</td>
<td>77</td>
<td>0.040</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>FeCl₃</td>
<td>100 mg/L pH 4</td>
<td>75</td>
<td>0.068</td>
</tr>
<tr>
<td>Poly-ferric sulphate</td>
<td>[Fe₂(OH)ₙ(SO₄)ₚ(OH)ₚ/2]ₘ</td>
<td>100 mg/L pH 4</td>
<td>71</td>
<td>0.040</td>
</tr>
</tbody>
</table>

*Approximate based on example bulk chemical costs (per tonne) in Australia (Gebbie 2006).
less chlorine-reactive NOM which is not conducive to reduction of disinfection requirement through better treatment.

For treated Myponga Reservoir water, ferric chloride showed marginally lower THMFP than alum and also noticeably less than PFS (Figure 6(c)). The general trend is of rapid reduction of THMFP at the lowest dose with only marginal improvement for the increased coagulant dose, indicating that the highest THM forming fraction of the NOM is easily removed by all the applied coagulants. Under the best treatment conditions (Table 2), ferric chloride treated THMFP was lowest at 16 μg/L in the Myponga Reservoir, while PFS treated THMFP was higher at 45 μg/L. Overall, there was no particular advantage in the application of PFS for THM reduction when compared with ferric chloride but some compared with alum. Correlation of THM formation with organic character fractions suggests that the improved removal of the hydrophobic acids and especially hydrophilic charged material by ferric chloride coagulation may explain the reduced THMFP.

Ultimately, it is the mechanisms of coagulation that will provide a limitation to the effectiveness of treatment and therefore disinfection. While advanced coagulants may optimize the performance of coagulation in a broader range of conditions, some organic materials will remain recalcitrant necessitating alternative treatment technologies should additional removal be required to meet regulatory requirements.
CONCLUSIONS

When compared at equimolar concentrations, advanced coagulants were found to perform equally for DOC removal as traditional inorganic coagulants and did not necessarily target or improve removal of problematic organic components but did demonstrate improvements in broadening the conditions at which coagulation was effective. A clear relationship was evident between coagulant dose/pH conditions for enhanced coagulation and minimized metal residuals. Selected ‘second stage’ coagulants tested were equally capable of improvements in chlorine demand reduction in the water source examined but when coagulation conditions were optimized, alum and ferric chloride were more effective for reducing THM formation. In each case (alum, ferric chloride and PFS), chlorine demand appeared to reduce proportionately to treated water DOC concentration; however the THM formation potential reduction diminished with increasing dose. In order to achieve further reductions in removal of recalcitrant organic material, additional treatment will be required and many treatment plants already take advantage of multiple step treatments, including coagulation, to remove problematic components in the treated water. While alternative technologies and multi-step treatments are bringing further improvements in treated water quality, coagulation remains a well developed and cost effective means of water treatment, with continuing relevance into the foreseeable future.

REFERENCES


First received 7 August 2011; accepted in revised form 26 April 2012